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DESALINATION OF SEAWATER USING CALCINED HYDROTALCITE WITH DIFFERENT MG/AL RATIO

Daiki Tsutsui[1] and Takaaki Wajima[2]
1-33, Yayoi-cho, Inage-ku, Chiba, Japan
[1,2]Department of Urban Environment Systems, Chiba University, Chiba, Japan
**corresponding author: [1]afga9263@chiba-u.jp; [2]wajima@ tu.chiba-u.ac.jp*

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ABSTRACT

Salt damaged farmland increases in the world, and a novel method to capture salt in soil for avaiable use of agriculture is desired. In this study, we focused on calcined hydrotalcite as a desalination agent, and desalination properties of calcined hydrotalcite with different Mg/Al ratio from seawater was estimated. Calcined hydrotalcite with Mg/Al ratio of 1 – 6 was prepared, and the desalination ability were investigated using seawater collected from an Imari bay in Saga prefecture, Japan. In comparison, commercial hydrotalcite was done as the same procedure. As a resalt, the decrease of salinity was confirmed using all calcined hydrotalcites and the decreasing rates were almost same. The calcined hydrotalcite with approximately Mg/Al = 3.0 indicated the highest desalination property, due to the decrease of Na^+, Mg^{2+}, Cl^- and SO_4^{2-} with addition of calcined hydrotalcite. The structure of calcined hydrotalcite returned to that of hydrotalcite by reconstruction reaction.

Keywords: *Seawater; Desalination agent; Calicined hydrotalcite; Mg/Al ratio.*

1. INTRODUCTION

In the twenty-first century, global environmental issues are very serious, and effective utilization of energy and mineral resource and the securing of food and water are urgent problems (Central Environment Council, 2011). Now, approximately 20 % of farmland in the world becomes salt damage soil with unsuitable properties for agriculture (Smith, 2015). Production of a stable supply of food is essential to sustain human life. Securing farmland is one of the most important factors in food production. Due to the global population growth, the demand for food is increasing (Sumida, 2015). Furthermore, in 2011, great earthquake occured in Tohoku area of Japan. Tsunami occurred, and farmland in Tohoku was damaged by seawater. A lot of farmlands are damaged by salt, and it is desired to improve the salt – damaged soil into plantable soil (Goto & Inagaki, 2012). There are some desalination methods, such as leaching, elution, disposal of outer layer soil, and salt absorption due to the halotolerant plant (Terasaki, 2013).

Now, leaching method, which makes farmlands good water permeability and flush out salinity with water, is a popular desalination method to improve salt - damaged farmlands. However, it takes a long time to improve perfectly, because it depends on weather (Japanese Society of Soil Science and Plant Nutrition, 2012). There are some studies to improve salt – damaged soil rapidly. For example, electorostatic desalination was studied, but this technology is not practical and it is expensive to use a large space (Takagi & Karita, 1995).

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Desalination using sorbent material is considered as eco-desalination technology due to the low operation cost as well as more friendly to the environment (Chakraborty, Sirshendu, DasGupta and Basu, 2005; Hu, Qiao, Haghseresh, Wilson and Lu, 2006; Yousef, El-Eswed and Al-Muhtaseb, 2011; Wibowo, Rokhmat, Sutisna, Khairurrijal, Murniati & Abdullah, 2015). In this process, undesireable substances are adsorbed by sorbent material. Although the concentration of undesired elements is slightly reduced by repeating the flow of feed water into the sorbent material, agreat reduction of undesirable substances might be obtained (Wajima, Shimizu, Yamato & Ikegami, 2010).

In this study, we focused on calcined hydrotalcite as a new salt damaged soil improving agent. In our previous study, calcined hydrotalcite could desalinate seawater and the solution could use for plant growth (Wajima, 2014). Hydrotalcite is Mg/Al type layered double hydroxide (LDH) known as inorganic anion exchangers. LDH expresses in $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}_{x/n} \cdot mH_2O]$ (M^{2+} : divalent metal ions, M^{3+} : trivalent metal ions, A^{n-} : anionic species, x = 0－1), and composed of metal complex hydroxide (Kameda, Yoshioka, Umezu & Okuwaki, 2005). The uptake of anions onto hydrotalcites from aqueous solution was occurred by two mechanisms (1) intercalation by anion exchange; (2) intercalation by reformation of calcined samples (Hibino, 2008). Intercalation by anion exchange was used for the removal of the anion or oxi - anions, such as sub-arsenic acid ion, etc., from water solution (Gillman, 2006). Intercalation by reformation of calcined LDH was also used for anion removal ,e.g. adsorption of vanadium (V) and NO_3^{2-} (Wang, Cheng, Wang, & Ma, 2012). However, little information can be available on desalination property of calcined hydrotalcite.

Therefore, the objective of this study was to investigate the desalination properties of calcined hydrotalcite from seawater in order to use as desalination agent.

2. EXPERIMENTAL

2.1 Preparation of Calcined Hydrotalcite

Five kinds of calcined hydrotalcite with different Mg/Al ratio (Mg^{2+} : Al^{3+}=1－5) were prepared as follow (Figure 1). The mixed solution (0. 1 – 0. 5 mol Mg^{2+} and 0. 1 mol Al^{3+}) was prepared using $Mg(NO_3)_2$ and $Al(NO_3)_3$ to synthesize the product with 1 – 5 of Mg/Al molar ratio. The Mg/Al mixed solution was quantitatively added to $NaNO_3$ solution at pH 12.5 under stirring at 50 ℃. In order to maintain pH of the solution (12.5), NaOH solution was slowly dropped in the stiring solution. The mixed solution was stirred for 6 hours with hot stirrer, and then solid products were obtained by a vacuum filtration method. The filtrated product washed with distilled water and then dried at 50 ℃ overnight. The obtained samples are indicated as HT1 – HT5, whose number is the Mg/Al molar ratio in the mixed solution during the synthesis. The calcined product obtained by heating each product at 450 ℃ for an hour in an electric furnace (Shigi, Tsuda, & Onishi, 2013; Wajima & Ikegami, 2010). The calcined products are also indicated as CHT1 – CHT5.

Identification of crystal structure of the product was carried out with a X-ray diffraction (XRD) equipment (Rigaku, MiniFlex 600). Mg/Al ratio in the structure were investigated as follow. 0.1 g of samples were dissolved in 10 mL of 1 M HCl solution by shaking for 24

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hours, and then the concents of Mg and Al in the solution were analyzed with atomic absorption spectrometry (Perkin Elmer, AAnalyst 200) to calculate the Mg/Al molar ratio of the samples.

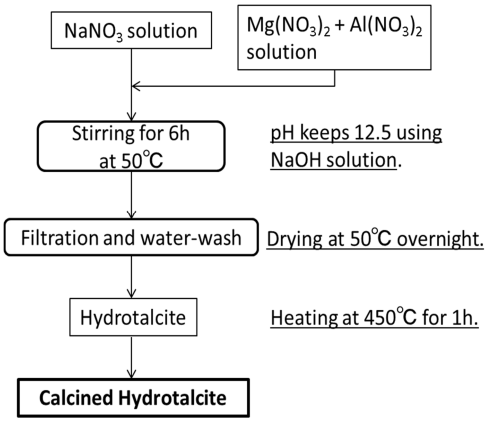

Figure 1: Flow chart of the experiment

2.2 Desalination Experiment

The desalination abilities of each product were investigated using seawater obtained from the surface of Imari bay, Saga prefecture, Japan. The chemical composition of seawater used in this study is shown in Table 1.

0.1 g of each calcined product was put into 5 mL of seawater in 50 mL of centrifuged tube and shaked for 5 hours. After shaking, salinity of seawater treated with calcined hydrotalcite were measured by salinity concentration meter (Lutron, YK – 31SA). The samples after the experiment were collected by filtration and analyzed by XRD equipment. The salinity of seawater after experiment were measured by Ion chromatograph (Tosoh, IC - 2010). In addition, commercial hydrotalcite was done the same experiment as comparison (Kyowa Chemical Industry Co., Ltd., KW500).

The amount of each ions removed by calcined hydrotalcite, q (mmol/g), was calculated using the following equation :

$$q = \frac{(Co - C) \cdot V}{w} \quad (1)$$

where C_0 and C are the concentrations (mmol/L) of each ions in the initial solution and the bind solution, respectively. V is the volume (L) of the solution, and w is the weight (g) of the sample added to the solution.

The removal percent of salt after treating seawater with each calcined products, R (%), was calculated using the following equation:

$$R = \frac{(Co - C)}{Co} \times 100 \quad (2)$$

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3. RESULTS AND DISCUSSION

3.1 Preparation of Calcined Hydrotalcite

Chemical compositions and the XRD patterns of the obtained products are shown in Table 1 and Figure 2, respectively. In all products, hydrotalcite peaks were confirmed and we succeed to prepare hydrotalcite product with different Mg/Al molar ratio (2.29 - 5.32). Therefore, calcined hydrotalcites with different Mg/Al molar ratios for desalination test from seawater was prepared from these hydrotalcite samples.

Table 1: chemical composition of hydrotalcite prepared in this experiment.

	Content (mmol/g)		Mg/Al molar ratio
	Mg	Al	
HT1	9.52	4.16	2.29
HT2	9.58	4.02	2.38
HT3	9.82	3.48	2.82
HT4	11.36	2.94	3.86
HT5	12.25	2.30	5.32
Commercial HT	10.62	3.54	3.00

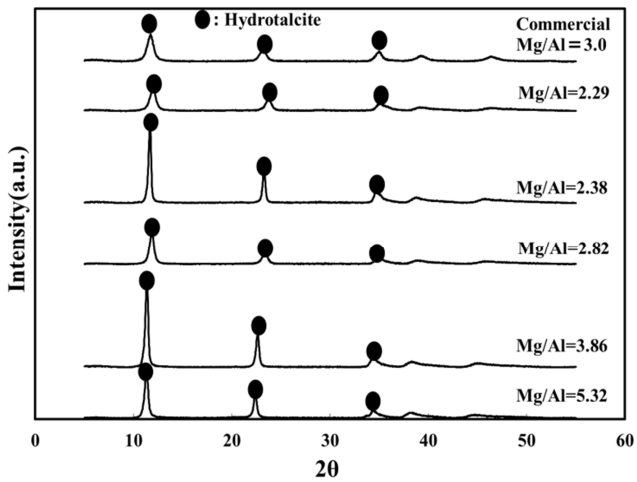

Figure 2: XRD pattern of the products and commercial hydrotalcite

The XRD patterns of calcined product are shown in Figure 3. In all calcined products, Mg – Al oxide peaks were confirmed and peak intensity increases with increasing Mg/Al ratio of

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calcined hydrotalcite, regardless of the peak intensity of hydrotalcite before calcination. It is because the Mg-Al oxide is mainly MgO.

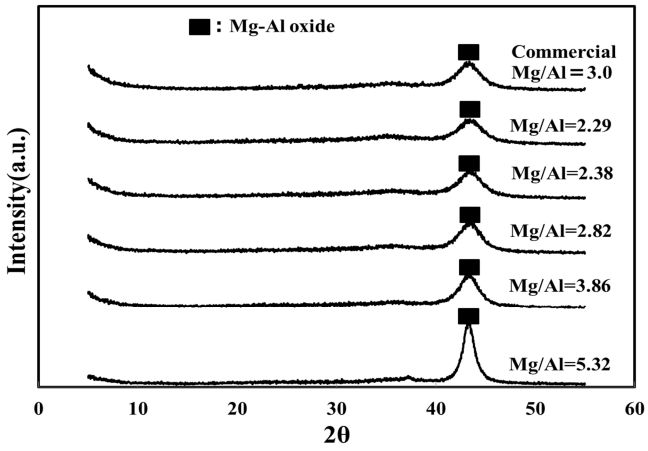

Figure 3: XRD pattern of the products and commercial hydrotalcite after calcination

3.2 Desalination Ability Of Calcined Products

The salinity and removal percent of salt after treating seawater with each calcined products are shown in figure 4. The salinity decreased in all seawater after treatment with calcined hydrotalcite. The highest removal of salt from seawater is treated with the product with approximately mg/al = 3.

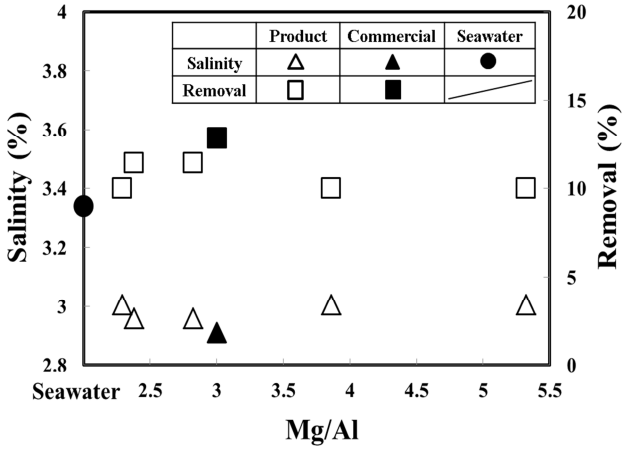

Figure 4: the salinity and removal of seawater treated with 6 products and commercial hydrotalcite after calcination

The chemical composition of seawater and the solution treated with calcined hydrotalcite are shown in table 2. Contents of na^{+}, mg^{2+}, ca^{2+} cl^{-} and so_4^{2-} decrease, while k^{+} is almost constant, with addition of calcined hydrotalcite. Especially, high amounts of cl- ions decrease using the product with mg/al ratio = approximately 3 – 4.

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Table 2: chemical composition of seawater and the solution treatment with calcined hydrotalcite

	Chemical composition (mg/L)					
	SO_4^{2-}	**Cl^-**	**Na^+**	**K^+**	**Mg^{2+}**	**Ca^{2+}**
Seawater	2801	22482	10186	359	1379	330
CHT1	1221	21077	10015	377	840	348
CHT2	1338	21173	10076	382	781	149
CHT3	1695	20552	10050	381	842	111
CHT4	2193	20396	9829	376	1456	0
CHT5	2253	20602	9905	378	1129	52
Commercial CHT	1546	18494	9105	349	665	85

Removal amounts of each elements in seawater by calcined hydrotalcite are shown in figure 5. For anions, removal amounts of so_4^{2-} in seawater after treated with calcined products decrease with increasing mg/al ratio of the product, while removal amounts of cl^- increase with increasing mg/al ratio to 3, and be almost constant above mg/al ratio to 3. We think difference of mg/al ratio cause difference of layer intervals. So the removal amounts are relevant to layer intervals.

For cations, removal amounts of mg^{2+} increase with increasing mg/al ratio to 3 and decrease above mg/al ratio = 3. Removal amounts of na^+ and ca^{2+} are almost constant values, and that of k^+ is almost zero regardless of mg/al ratio of the product. They were caused by increasing ph of the seawater. When we added the calcined products in the seawater, ph were increased to about 10. So we think a lot of cations were connected with anion and crystallize.

These results suggest that calcined hydrotalcite can decrease salinity of seawater due to the removal of cl^- and mg^{2+} from seawater.

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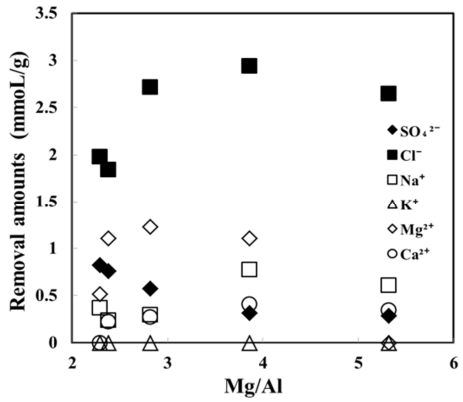

Figure 5: Removal amounts of each elements in seawater by calcined hydrotalcite.

3.3 Reconstraction Reaction Of Calcined Products

Xrd patterns of the product after desalination tests are shown in figure 6. For all products, the structure of calcined hydrotalcites returned to that of hydrotalcite by reformation reaction. It was confirmed that all product remove salts in seawater by reformation reaction.

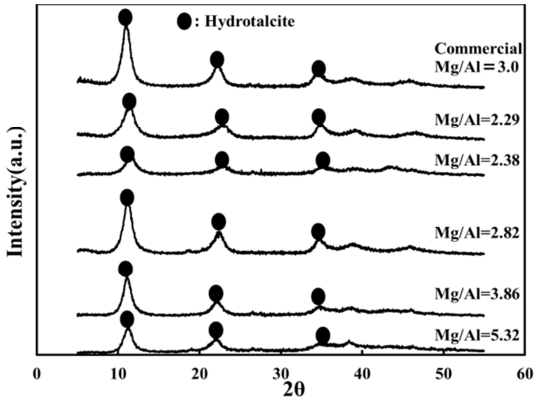

Figure 6: XRD pattern of the products and commercial hydrotalcite after desalination test

Intensity of peaks for the face (003) of hydrotalcite after desalination test is shown in Figure 7. With increasing mg/al ratio of the product to 3, the intensity of hydrotalcite peaks after desalination increase, and above mg/al = 4 of the product, those decrease, which is good accordance with desalination behavior, indicating in Fig. 4.

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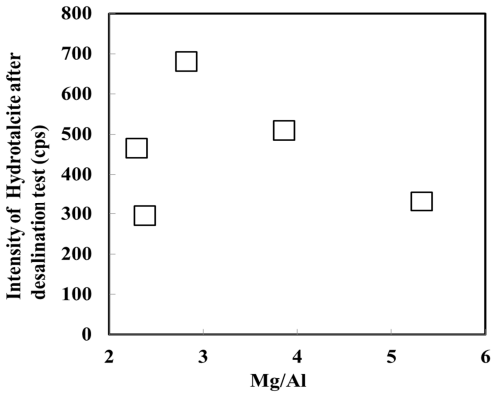

Figure 7: Intensity of peaks for hydrotalcite after desalination test.

From this result, hydrotalcite with approximately mg/al = 3 have the highest desalination property, due to the structure reformation reaction in solution to remove na^{+}, ca^{2+}, mg^{2+}, cl^{-}, so_4^{2-}, especially cl^{-} and mg^{2+}.

4. CONCLUSION

In this study, we investigated the desalination properties of calcined hydrotalcite by the reformation process. As a result, Mg – Al oxide peak in all calcined products confirmed and peak intensity of Mg/Al oxide increased with increasing Mg/Al ratio of the product. The salinity decreased in the all seawater after treatment with calcined hydrotalcite. The highest desalination from seawater were treated with the product with approximately Mg/Al = 3, because the structure of calcined hydrotalcite can remove high amounts of Cl^{-} and Mg^{2+} from seawater by reformation reaction.XRD patterns of the obtained product are shown in Fig. 3. It is noted that Mg/Al molar ratio of each product indication.

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